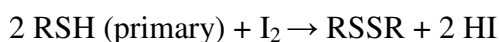**INDIANA DEPARTMENT OF TRANSPORTATION**
OFFICE OF MATERIALS MANAGEMENT

MERCAPTANS (WATER INSOLUBLE)
BY
IODIMETRIC TITRATION-DEADSTOP
ITM No. 602-15T

1.0   SCOPE.

1.1   This method of test covers the procedure for the iodimetric oxidation of the primary mercaptan group to the disulfide:

$$2 \, RSH \, (primary) + I_2 \rightarrow RSSR + 2 \, HI$$

The endpoint is detected by a deadstop procedure using as the titrant a solution of iodine in benzene. A solvent system of pyridine-benzene is used to dissolve the sample and iodide in water to initiate the electrode response.

1.2   This ITM may involve hazardous materials, operations, and equipment and may not address all of the safety problems associated with the use of the test method. The user of the ITM is responsible for establishing appropriate safety and health practices and determining the applicability of regulatory limitations prior to use.

2.0   REFERENCES.

2.1   AASHTO Standards.

M 231   Weighing Devices Used in the Testing of Materials

2.2   ASTM Standards.

D 1193   Reagent Water
E 203   Water Using Volumetric Karl Fischer Titration
E 287   Laboratory Glass Graduated Burets
E 960   Laboratory Glass Beakers
E1272   Laboratory Glass Graduated Cylinders

2.3   American Chemical Society Standards.

Reagent Chemicals

3.0   TERMINOLOGY. Definitions for terms and abbreviations will be in accordance with the Department's Standard Specifications, Section 101.

4.0   SIGNIFICANCE AND USE. This ITM is used to determine quantitatively the amount of primary mercaptans contained in the hardener component of polysulfide epoxy penetrating sealers. The mercaptan provides additional flexibility to the cured epoxy penetrating sealers which are used to protect the PCC bridge decks against chloride penetration.

5.0   APPARATUS.

    5.1   Buret, 25 mL, Class A, in accordance with ASTM E 287

    5.2   Beaker, Type I, in accordance with ASTM E 960

    5.3   Karl Fisher Titration assembly or equivalent with single dual platinum electrode in accordance with ASTM E 203

    5.4   Magnetic stirrer and teflon covered stirring bar

    5.5   Balance, Class A, in accordance with AASHTO M 231

    5.6   Graduated cylinders, Class A, Style I, in accordance with ASTM E 1272, and calibrated to deliver

    5.7   Miscellaneous laboratory equipment as required

6.0   REAGENTS.

    6.1.   Reagents. Unless otherwise indicated, all reagents shall conform to the specification of the Committee on Analytical Reagents of the American Chemical Society when such specifications are available. Other grades may be used, provided that the reagent is of sufficiently high purity to permit the use of the reagent without lessening the accuracy of the determination. Also, the analyst may ensure the accuracy of the results by testing blanks or checking against a comparable sample of known composition.

        6.1.1   Iodine, Reagent Grade

        6.1.2   Benzene, Reagent Grade

6.1.3   Pyridine, Reagent Grade

6.1.4   Potassium Iodide, (Iodate Free), Reagent Grade

6.2   Water.   Unless otherwise indicated, references to water are understood to mean reagent water Type II in accordance with ASTM D 1193

6.3   Reagent Solutions.

6.3.1   Iodine in Benzene, 0.05N, Dissolve 3.1728 g of reagent grade Iodine per liter of reagent grade benzene.

6.3.2   Pyridine-Benzene Solution, 60/40 % by volume, mix 40 mL of reagent grade pyridine with 60 mL of reagent grade benzene for each 100 mL of solution.

6.3.3   Potassium Iodide Solution, aqueous 2 % by weight, Dissolve 2 ± 0.005 g of reagent grade potassium iodide in water and dilute to 100 mL.

7.0   PROCEDURE.

7.1   Add 100 mL of a 60/40 (by volume) pyridine-benzene solution using a graduated cylinder to a 250 mL beaker

7.2   Use a graduated cylinder to add 10 mL 2 % aqueous potassium iodide solution

7.3   Insert dual platinum electrode into solution leaving space for magnetic stirrer

7.4   Set sensitivity of titration assembly microammeter to desired level by titration with 0.05 N I_2 in benzene (See Supplementary Information)

7.5   Add to the test solution a sample of 0.5 g ± 0.1000 g.   The sample size is determined by weighing a shell vial containing the material to be analyzed, pouring a small amount into the test solution, and reweighing the shell vial.

7.6   Refill the buret to capacity with 0.05 N I_2 in benzene. Titrate the test solution to the microammeter reading previously established in 7.4, using the magnetic stirrer. As the endpoint is approached, the test solution shall appear to change from a clear condition to a yellowish tint.   The microammeter needle may momentarily exceed the target setting, but shall return to the target setting upon the addition of another drop or two of titrant. Should gross over-titration occur, add another 0.5 g. sample to the test solution and retitrate, using the combined sample weights as a calculations base.

7.7   Record   mL   of   0.05   N I_2 consumed

8.0   SUPPLEMENTARY INFORMATION.

    8.1   To adjust the microammeter to a proper sensitivity of needle response, a sufficient amount of 0.05 N I_2 in benzene is titrated into the test solution (7.4) to yield a reading of about 15 µA. To avoid a condition of excessive circuit resistance, the amount of I_2 solution added at this point should not exceed 0.4 mL.

    8.2   At the beginning of 7.4, the electrodes are in a polarized condition and current flow is impeded. With the addition of a small amount of iodine, the electrodes are depolarized and the current flow registers on the ammeter. Upon addition of the sample, electrode polarization again occurs and current flow is impeded until introduction of an excess of iodine results in electrode depolarization at the pre-selected end point.

    8.3   The solvent system shall contain water with potassium iodide otherwise no electrode response shall occur or erratic meter needle fluctuations are encountered.

    8.4   No more than two consecutive determinations shall be run in each solvent system.

9.0   CALCULATIONS.

    9.1   Calculate % SH as follows:

$$\% \, SH = \frac{(mL \, I_2 \, (N \, I_2)) \, x \, 3.31}{Weight \, of \, sample, \, g}$$

10.0   REPORT. Test results are reported to the nearest 0.01 % in the range 0 - 20 % and to the nearest 0.1 % for results above 20 %.

11.0   PRECISION. Limited data indicate the precision to be on the order of ± 0.3 % relative.